electronic structure, as indicated by the interpretation of the electronic spectrum.[6]

The average Ru–Br bond length (2.53 (3) Å) is, as expected, about 0.12 Å longer than the equivalent distance in the chlorine complex.[8] This leads to an increase in the Ru–Ru distance [2.852 (4) Å, cf. 2.753 (4) Å]. The increase is moderated by a slight closing in the Ru–Br–Ru angle (average 68.5°, cf. 70.2°) suggesting the presence of a Ru–Ru interaction. The average Ru–N distance (2.08 (4) Å) is smaller than that found in the chlorine complex (2.11 Å),[8] but the precision of both determinations is low so the difference is not significant.

This appears to be the first structure report of a mixed-valence Ru^{II}–Ru^{III} dimer with a tribromo bridge. There have been several structures published over the last few years of Ru^{II}–Ru^{III} dimers with trichloro bridges.[8,13–15] In addition, there are many known trihalo-bridged Ru^{II}–Ru^{II} compounds with phosphine and arsine ligands.[16] The structures of these and of other related compounds which have been determined, however, all appear to be of the trichloro species.[16–19] The only structural characterization of a dimer with a tribromo bridge appears to be that of the Ru^{III}–Ru^{III} dimer $[Ru_2Br_9]^{3-}$ determined by powder diffraction.[20] Mixed-valence states of this species have been generated electrochemically,[21] but do not appear to have been structurally characterized.

Finally, although the tris(μ-halo) dimeric structure appears to be common for ruthenium complexes, other possibilities must be considered. Bino and Cotton[22] have described a linear, trinuclear Ru^{III}–Ru^{II}–Ru^{III} complex with two tris(μ-chloro) bridges, $[Ru_3Cl_{12}]^{4-}$. And the tris(ethylenediamine)ruthenium(II) ion can react with hydrohalic acids to form intense blue species.[23] Because of the bidentate nature of the ethylenediamine ligand, these are unlikely to be structurally analogous to the compound described in this article. Further work on such compounds would be desirable in view of the biological activity of the chloro-bridged compound.[24,25]

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Registry No. $[Ru_2(NH_3)_6Br_3](ZnBr_4)$, 114094-47-2; $[Ru_2(NH_3)_6Br_3]Br_2$, 58320-17-5.

Supplementary Material Available: Tables SI and SII, listing thermal parameters and the restrained hydrogen positional and thermal parameters (1 page); a table of calculated and observed structure factors (5 pages). Ordering information is given on any current masthead page.

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Oxygen-17 NMR of Seven-Valent Neptunium in Aqueous Solution[1]

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Alkaline solutions of seven-valent neptunium in water enriched in oxygen-17 show a ^{17}O NMR resonance about 1470 ppm downfield from the solvent resonance. Measurement of relative areas indicates that the Np(VII) oxygen resonance contains about four oxygen atoms per Np atom. This result is interpreted in terms of the six-coordinated Np(VII) anion $NpO_4(OH)_2^{3-}$, in which four oxygen atoms are present in a square plane around the Np and are responsible for the observed resonance. The two hydroxyl groups are located further from the Np at the vertices of a tetragonal bipyramid and presumably exchange too rapidly with solvent oxygen for their ^{17}O resonance to be seen. The Np(VII) oxygen resonance has a line width that increases with temperature and is around 400 Hz at 25 °C. The temperature dependence of the line width can be accounted for by a process of oxygen exchange between the Np(VII) species and the solvent, with a pseudo-first-order rate constant of about 10^3 s^{-1} at 25 °C. No Np(VI) oxygen resonance was observed in alkaline solution, probably because the Np(VI) oxygens exchange too rapidly with the solvent.

Introduction

Although Np(VII) has been known since 1967, considerable doubt still remains regarding the form in which it exists in aqueous solutions. Potentiometric measurements have shown the electrode potential of the Np(VI)–Np(VII) couple to increase as (RT/F) log $[H^+]^2$ in acid solution[2] and to decrease as (RT/F) log $[OH^-]^2$ in base.[3,4] Since the form of Np(VI) in acid solution has been established to be NpO_2^{2+}, this implies that the Np(VII) species in acid has a charge of +1. The nature of Np(VI) in alkaline solution has not been well established, because of its low solubility. The authors of the potentiometric studies assumed it to be NpO_4^{2-} or $NpO_2(OH)_4^{2-}$, and they therefore concluded that the Np(VII) species in base had a charge of −3.

In any case, these measurements do not establish the actual coordination number of the Np(VII) species. The conventional wisdom seems to be that Np(VII) exists in the form NpO_3^+ in acid and in the form $NpO_4(OH)_2^{3-}$ in base.[5] The latter conclusion is supported by the observation that salts containing six-coordinated Np(VII) can be isolated from alkaline solution.[6–8]

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Oxygen-17 NMR is, at least in principle, capable of shedding further light on the nature of aqueous Np(VII). If the oxygens bound to the Np(VII) exchange with solvent oxygen at a rate that is small compared to the magnitude of their chemical shift, the ^{17}O NMR spectrum of aqueous Np(VII) solutions should show two distinct resonances, corresponding to the two types of oxygen, and the ratio of the areas of these resonances should permit calculation of the number of oxygen atoms coordinated to the neptunium. Oxygen exchange between neptunium species and solvent has only been measured for five- and six-valent neptunium in acid solution,[9,10] where it is moderate to rapid for Np(V) and slow for Np(VI). In acid, however, Np(VII) is a very powerful oxidant, and its reaction with water proceeds too rapidly for NMR measurements to be practical. It is only feasible to carry out such measurements in base, where nothing is known about the exchange rates of Np(V) and Np(VI). Nevertheless, it does not seem unreasonable to hope that oxygen exchange between Np(VII) and solvent in base will be slow enough to permit a meaningful NMR study. Furthermore, since Np(VII) is the only diamagnetic neptunium valence state, it should be particularly suitable for such a study.

These considerations have led us to undertake the present oxygen-17 NMR study of neptunium(VII) in alkaline solution.

Experimental Section

Preparation of Samples. Two different approaches were used to prepare samples of Np(VII). In one, the Np(VII) salt Li_5NpO_6 was made by a dry technique[11] and dissolved in water or base. In the other, Np(V) was oxidized in strong base by hypobromite.[12]

To synthesize Li_5NpO_6, NpO_2 was mixed in a drybox with sufficient Li_2O_2 to provide slightly more than 5 mol of Li/mol of Np. The mixture was ground in an agate mortar and placed in an alumina boat, which was then inserted into a fused silica tube inside a furnace. The mixture was heated at 400 °C for 24–72 h in a stream of oxygen, after which it was cooled, analyzed, reground, and reheated. The procedure was repeated until analysis showed a constant content of Np(VII), about 80–85% of the total neptunium. This material is designated "Li_5NpO_6" throughout this paper, to call attention to the fact that it is not a pure material.

For NMR measurements, the "Li_5NpO_6" was dissolved in water or dilute NaOH that was about 10 mol % $H_2{}^{17}O$ and about 20 mol % DOH. In some cases, the solutions were subsequently treated with ozone to increase the content of Np(VII). Solid material was removed by centrifugation.

For oxidation of Np(V) with hypobromite, a freshly prepared hydrous neptunium(V) oxide precipitate was slurried with a solution of LiOH and Br_2 in water that was enriched with both oxygen-17 and deuterium. The slurry was heated for 4 h in a water bath at 60–80 °C, after which it was centrifuged, and the supernatant solution was analyzed and transferred to an NMR tube. Reagent concentrations were chosen to give the following final concentrations: [LiOH] = 2–3 M, [LiOBr] = 0.1–0.15 M, [Np(VII)] = 0.1–0.15 M, [$H_2{}^{17}O$] = 10 mol %, and [DOH] = 10–20 mol %. Analysis indicated complete oxidation of the neptunium to Np(VII) within the accuracy of the method (about ±2%). In one experiment the hydrous neptunium(V) oxide was prepared from an acidic Np(V) solution in 10 mol % $H_2{}^{17}O$ that had been heated to ensure complete exchange of the neptunyl oxygens.

A few reference experiments were carried out in which potassium chromate took the place of neptunium. Potassium dichromate was dissolved in enriched water and allowed to reach isotopic equilibrium before NaOH was added to convert the Cr(VI) entirely to CrO_4^{2-}.

Analytical Procedures. Neptunium(VII) concentrations were determined spectrophotometrically in 1 M NaOH from the Np(VII) absorbance at 618 nm (ϵ_{max} = 393 M^{-1} cm^{-1}).[13] Whenever possible, the NaOH solution was first treated with a very small amount of Np(VII), and the increase in absorption at the maximum that resulted from addition of a second and larger portion of Np(VII) was used to determine the concentration. The method was validated by comparison with the method in which Np(VII) is determined by reaction with Cr(III), followed by spectrophotometric determination of the Cr(VI) that is formed.[14]

Total neptunium was determined spectrophotometrically as Np(V) after reduction with nitrite in 1 M perchloric acid. The extinction coefficient at the 980-nm maximum was taken to be 403 M^{-1} cm^{-1} when measured with a spectral bandwidth of about 1 nm.[15] All spectrophotometric measurements were made with a Cary 14 spectrophotometer.

NMR Measurements. Samples for NMR measurements were placed in 10 mm o.d. glass tubes fitted with Teflon liners. Solution volumes of 1–1.5 mL were used. The Teflon liners were not employed for chemical reasons but rather to provide secure containment of the radioactive sample in the event of tube breakage.

Measurements were made with a Bruker AM-300 NMR spectrometer operating at 40.7 MHz, with quadrature detection and a deuterium lock. Typical measurement conditions were as follows: spectral width = 83 333 Hz, pulse width = 5–10 μs (30–60°), delay before acquisition = 7.5–100 μs, acquisition time = 0.098 s, repetition rate = 10/s, digital resolution = 10 Hz/point, line broadening = 10 Hz, and total accumulation = 10 000 transients. A few survey experiments were carried out with a 167 000-Hz spectral width, 5-μs pulse width, and 40 Hz/point digital resolution. For these experiments a postacquisition delay was added to slow the repetition rate to about 10/s. The room-temperature reference experiments in which chromate was substituted for Np(VII) were carried out with spectral width = 41 667 Hz, acquisition time = 0.196 s, digital resolution = 5 Hz/point, and line broadening = 3–5 Hz.

Samples were spun at about 12 rpm in a thermostated probe assembly. Temperature was controlled with the proportional temperature controller associated with the spectrometer. Subambient temperatures were achieved by supplemental cooling with a stream of nitrogen gas that had been chilled by passage through a copper coil immersed in liquid nitrogen. The probe temperature indicator was calibrated by comparing its readings with those of a thermocouple immersed in water in a tube identical with the ones used for the neptunium samples. Nevertheless, variations in gas flow and position of the temperature sensor may cause reported temperatures to be in error by as much as 1 °C.

The chemical shifts of the Np-containing species were determined with respect to the resonance of the solvent oxygen. No attempt was made to measure changes in the position or width of the solvent resonance.

Area and Line Width Calculations. Areas and line widths were determined graphically from expanded plots of the individual resonances. This rather old-fashioned approach was found to give more reproducible results than could be obtained by use of the digital manipulation routines provided with the spectrometer. The measured full widths at half-maximum, $W_{1/2}$, were corrected by subtraction of the line-broadening factor (usually 10 Hz). Relaxation times derived from the corrected line widths were used to correct the areas of the resonance peaks for decay during the preaquisition delay interval. In a few experiments, trifluoroacetate was introduced as an internal standard. We found, however, that more consistent results could be obtained by comparing the area of the sample resonance to that of the solvent. Ratios of areas were corrected for the effects of finite pulse power, under the assumption that the power distribution, $P(\nu)$, was symmetrical around the center of the spectrum and followed the relationship[16]

$$P(\nu) = [P(\nu_0)](\sin [\pi t|\nu - \nu_0|])/\pi t|\nu - \nu_0|$$

where ν is the frequency in hertz, ν_0 is the frequency of the center of the spectrum, and t is the pulse width in seconds. This correction was minimized by placing the center of the spectrum as near as possible to the midpoint between the sample and solvent peaks. The correction amounted to about 2% for 5-μs pulses and about 7% for 10-μs pulses. The corrected area ratios showed no systematic dependence on pulse width, implying that the correction was at least approximately correct and indicating that the pulse repetition rate was sufficiently low in relation to T_1 to allow complete spin relaxation between pulses. Area ratios also showed no systematic dependence on the line-broadening factor that was applied.

Area ratios were converted to oxygen atom ratios through the use of measured concentrations and solution densities. We made the assumption that the molar volume of water was independent of its isotopic composition.

Results

Neptunium(VII) shows a single well-defined oxygen-17 resonance about 1470 ppm downfield of the H_2O solvent resonance. This resonance of oxygen on neptunium(VII) has reached its

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Table I. ^{17}O NMR Data for Np(VII) Solutions: Line Widths and Relative Peak Areas

T, K	W,[a] Hz measd	W,[a] Hz calcd[b]	R[c]	n[d]
	0.075 M Np(VII) in 0.45 M NaOH[e,f]			
273.4	143	145		
284.5	191	185		
297.2	331–338	339		
306.5	570	573		
315.4	975	955		
	0.170 M "Li_5NpO_6" [0.138_5 M Np(VII) + 0.031_5 M Np(VI)]			
273.4	159–166	161	82–88	
280.4	198–204	205	83–88	
288.7	300	301	78–82	
296.1	429–460	437	90–93	
304.4	684	672		
312.4	985	1012		
			86.5 ± 2.9[g]	4.7 ± 0.16[g]
	0.152_4 M Np(VII) in 2.8 M LiOH[h]			
273.4	242		79–84	
283.5	225		86–89	
294	342		93–97	
			88.3 ± 5.4[g]	4.2_5 ± 0.24[g]
	0.110 M CrO_4^{2-} in 1.4 M NaOH[f]			
273.4	25		109	
294–296	12		107–114	
			109.7 ± 4.0[g]	4.5 ± 0.17[g]

[a] Full width at half-maximum of resonance of oxygen bound to Np(VII) at ca. 1470 ppm downfield from solvent resonance, or that of oxygen bound to Cr(VI) at ca. 812 ppm downfield from solvent. Ranges of measured values indicate variation in replicate measurements on the same sample and probably reflect temperature fluctuations. [b] Calculated from least-squares analysis. See text. [c] Ratio of area of solvent oxygen resonance to area of resonance of oxygen bound to Np(VII) or Cr(VI). Ranges indicate variation in replicate measurements on the same sample. [d] Number of atoms of oxygen bound to each atom of Np(VII) or Cr(VI). [e] Made by dissolution of "Li_5NpO_6" in aqueous NaOH followed by ozonation. [Np(VI)] < 0.004 M. [f] Solution also contained 0.1 M $LiOC(O)CF_3$ as an internal standard. [g] Average value. Uncertainties are twice the standard deviation of the mean. [h] Solution also contained 0.5 M LiBr and 0.13 M LiOBr.

equilibrium value by the time of the first NMR measurement (about 20 min after mixing) and does not change thereafter. In order to search for resonances from "hidden" oxygen that might not exchange readily with the enriched solvent, Np(VII) was prepared from Np(V) that had been brought to isotopic equilibrium with enriched water. No additional oxygen resonances were observed. Nor was any evidence of an Np(VI) oxygen resonance found in an experiment in which about 0.03 M Np(VI) was present.

The experimental data on line widths and area ratios are summarized in Table I. In the first two series of experiments the width of the Np(VII) oxygen resonance increases markedly with increasing temperature. This effect is obscured in the third series by an overall broadening of the resonance, which may be due at least in part to the increased viscosity of the concentrated LiOH solution. It seems reasonable to attribute the increase of line width with temperature to chemical exchange, and we have attempted to interpret the observed widths as the result of a combination of an intrinsic transverse relaxation time, T°_2, with one reflecting the chemical exchange:[17]

$$\pi W_{1/2} = 1/T^\circ_2 + 1/T^{ex}_2$$

The first term may be expressed in terms of the solution viscosity η and the absolute temperature T[18]

$$1/T^\circ_2 = 1/T^\circ_1 = K\eta/T$$

where K is a constant, while the second term may be equated to

Table II. Parameters Derived from Least-Squares Analysis of Line Widths[a]

	0.075 M Np(VII)[b] in 0.5 M NaOH	0.17 M "Li_5NpO_6"[c]
$1/T^\circ_2{}^{298.15}$, s^{-1}	138 ± 18	91 ± 19
$k_{ex}{}^{298.15}$, s^{-1}	980 ± 40	1440 ± 40
$\Delta H^\ddagger$, kJ/mol	46.6 ± 2.8	39.5 ± 2.4
$\Delta S^\ddagger$, J/(mol K)	−31 ± 9	−52 ± 8

[a] Kinetic parameters refer to a pseudo-first-order rate constant for exchange of all of the slowly exchanging O atoms in the Np(VII) moiety. Uncertainties are twice the standard deviations derived from the least-squares computation. [b] [Np(VI)] < 0.004 M. [c] 0.138_5 M Np(VII) + 0.031_5 M Np(VI).

the pseudo-first-order rate constant for the exchange process, k_{ex}, and may be written in the formalism of transition state theory

$$1/T^{ex}_2 = (kT/h)[\exp(\Delta S^\ddagger/R)]\exp(-\Delta H^\ddagger/RT)$$

Lacking further information, we have assumed that the solution viscosities varied with temperature in the same manner as does the viscosity of water, which follows the empirical relation[19]

$$\eta_{water} = 241.4\exp[570.58/(T-140)]$$

We have therefore carried out a three-parameter least-squares fit of the line-width data for each of the first two series of experiments to the overall expression

$$W_{1/2} = (A/T)\exp[570.58/(T-140)] + BT\exp(C/T)$$

These fits lead to the calculated line-width values in Table I and to the parameters shown in Table II.

Discussion

The ratios of peak areas given in Table I imply that the observed oxygen resonance of Np(VII) corresponds to somewhere between four and five oxygen atoms per neptunium atom. When we note further that the chromate reference experiments give a high oxygen/chromium ratio, we are strongly tempted to conclude that the results are indicative of an O/Np ratio of 4. We believe, however, that this conclusion should be drawn with some caution, in view of the substantial scatter in the data, the apparent dependence of the ratio on temperature in 2.8 M LiOH, and the ever present possibility of instrumentally induced artifacts. Comparison with the chromium results is not unequivocal, since the chromate resonance is very much narrower than that of the Np(VII) species.

Nevertheless, the conclusion that the Np(VII) oxygen resonance does in fact correspond to four oxygens per neptunium need not be inconsistent with other information regarding the nature of aqueous Np(VII). It seems highly unlikely that the predominant species is NpO_4^-, since the observed dependence of the Np(VI)–Np(VII) potential on hydroxide ion concentration[3,4] would then require that the Np(VI) be present as a neutral species, whereas electromigration studies have shown both Np(VI) and Np(VII) species to migrate as anions in alkaline solution.[3] But even if we accept the general belief that the Np(VII) is present as a six-coordinated ion of charge −3, it is not necessary to conclude that all of the oxygens in the coordination sphere of the neptunium are equivalent. In fact, in most of the six-coordinated Np(VII) compounds that can be obtained from aqueous solution,[6,7] the neptunium is surrounded by six oxygen atoms arranged as a tetragonal bipyramid. Four of these oxygen atoms form approximately a square plane, with a Np–O distance of about 1.9 Å, while the two remaining oxygen atoms are at the vertices of the bipyramid and have Np–O distances of 2.3–2.4 Å. The suggestion has been made that the square-planar NpO_4 group is stabilized by substantial double-bond character.[7] It therefore does not seem at all unreasonable to postulate that in the ion $NpO_4(OH)_2^{3-}$, four of the oxygens will give a distinct resonance, while the other two, which are in the form of hydroxyl groups, will be

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broadened out by extremely rapid exchange with solvent oxygen.

We interpret the increase of line width with temperature as being due to chemical exchange, and since there is no direct evidence of other species with which exchange can take place, we attribute the increase primarily to exchange with the oxygens of the solvent, with a room-temperature rate constant of about 10^3 s^{-1}. Since the form of the rate law for exchange has not been established, this is an overall pseudo-first-order rate constant. It applies to the rate for exchange of all of the slowly exchanging oxygen atoms in the Np(VII) moiety.[20]

The kinetic parameters given in Table II appear to differ significantly between the two solutions that were studied. An obvious difference between these two solutions is that the 0.5 M NaOH solution contained very much less Np(VI) than did the solution prepared by simply dissolving "Li_5NpO_6" in water. This is due partly to the ozonation of the NaOH solution, but probably more to the limited solubility of Np(VI) in 0.5 M NaOH. The rate of exchange appears to be significantly greater in the solution without NaOH, and it is possible that this increase results from an oxygen exchange between Np(VII) and Np(VI). It is interesting that $1/T^{\circ}_2$ is larger in the 0.5 M NaOH solution; i.e., the "intrinsic" line width in the absence of exchange is greater in such solutions. The crudeness of our kinetic analysis and the limited range of Np(VII) and base concentrations over which measurements can be made make it appear unprofitable to pursue these effects in greater detail or to attempt to deduce a complete rate law. In any case, the difference in parameters between the two solutions can be regarded as setting an upper limit to the rate of any Np(VI)–Np(VII) exchange.

It is noteworthy that we see no evidence of an Np(VI) oxygen resonance in the solution made by dissolving "Li_5NpO_6" in water, even though substantial amounts of Np(VI) are present. An Np(VI) oxygen resonance has been observed in acid solution about 2900 ppm downfield of the solvent,[21] and we have seen a similar resonance in carbonate solutions containing Np(VI). These observations would suggest that the Np(VI) oxygen resonance is broadened out in strongly alkaline solution, presumably by rapid exchange with solvent oxygen. (If Li_5NpO_6 dissolves to form $NpO_4(OH)_2^{3-}$, the resulting solution will necessarily be strongly alkaline, since it will contain two free hydroxide ions per neptunium.)

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Registry No. $NpO_4(OH)_2^{3-}$, 44442-28-6; Np, 7439-99-8.

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Notes

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A Carbon-to-Boron-Bridged Benzo-*o*-carborane

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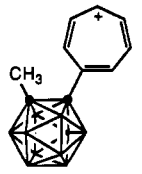
The electronic structure of hypervalent carbon has greatly interested chemists from very different fields, including organometallic, carborane, and cluster (carbide) chemistry, as well as carbocation chemistry.[1] Hypervalent carbon atoms are generally found in electron-deficient systems, where electrons are in short supply and thus have to be spread relatively thinly to hold molecules or ions together. Although the concepts of three-center–two-electron or multicenter bonding, pioneered by Lipscomb,[2] have been a great help in this area, the local bonding structures of some hypercarbons still puzzle chemists. This is especially true in icosahedral carborane chemistry. The organic chemistry of carboranes developed during the past two decades is largely confined to the carbons in the cage, and the number of these carbon-substituted carboranes, which include metallocarboranes containing carbon–metal bonds, has been ever growing.[3] Nevertheless, the electronic bonding structure of the two cage carbons in these molecules still remains ambiguous.

The theoretical treatment of icosahedral carboranes can be traced to early work by Hoffmann and Lipscomb in the 1960s.[4] Their elegant prediction of "superaromaticity" of carboranes has been successfully verified by experimental chemists.[3] Since the 1960s, carboranes have been often described as three-dimensional aromatic compounds in analogy to the two-dimensional benzene rings.[3] The demonstration of conjugation between a p orbital on a π substituent attached to the cage and a surface orbital of the polyhedron, as suggested by Hoffmann and Lipscomb,[4] however, has proven to be much more difficult. The measurements, by Hawthorne, Berry and Wegner,[5] of pK_a's for carboranylbenzoic acids and carboranylanilinium ions, and of ^{19}F NMR chemical shifts of carboranylfluorobenzenes, showed that the $-I$ effect of the *o*-carborane cage is similar in magnitude to that of the halogens, and that ground-state cage–ring π interaction is *not* important.[5] These authors also found that isomer ratios in nitration of 1-phenylcarborane (*o*:*m*:*p* = 4:26:70) indicate electron donation by the cage in the transition state for nitration.[5] However this $+T$ effect could not be observed when UV and ^1H NMR spectra of the 1-methyl-2-tropenyliumylcarborane cation **1** were studied.[6]



1

The results from UV and Raman spectra of phenylcarboranes

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